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ISOMERIZATION OF 1-BROMOPENTABORANE(9) BY BASE CATALYSIS

by

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ISOMERIZATION OF 1-BROMOPENTABORANE(9) BY BASE CATALYSIS [1]

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Sir:

The reversible conversion of 1-BrB_5H_8 [2] to the previously unknown and far more volatile isomer 2-BrB_5H_8 is catalyzed by hexamethylenetetramine. Also effective is dimethyl ether, but with side reactions qualitatively varying with temperature: one result is a new synthesis of 1-$CH_3B_5H_8$.

(2) T. Onak and G. B. Dunks, Inorg. Chem., 3, 1060 (1964) and earlier references there cited.

The relatively low volatility of 1-BrB_5H_8 would relate to the negative charge at the apex of the B_5H_9 skeleton; [3] and

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 110.

and the enhanced B-Br bond polarity would gain effect from a probable molecular packing with the apex bromine atom near to the four basal boron atoms of another molecule. Such packing would be inconvenient for 2-BrB_5H_8. The $CH_3B_5H_8$ isomers show a smaller and opposite difference of volatility.

Syntheses. Direct Al_2Cl_6-catalyzed bromination of B_5H_9 gave exclusively 1-BrB_5H_8, [2] but one experiment without any catalyst (12 hr., warming to 25°) gave a 4% fraction later recognized as 2-BrB_5H_8, with an 82% yield of 1-BrB_5H_8.

Isomerization. Freshly vacuum-sublimed $(CH_2)_6N_4$ (ca.

100 mg.) and 0.936 mmole of 1-BrB_5H_8 (20 hr., sealed tube, 35°) gave 0.461 mmole of 1-BrB_5H_8 and 0.454 mmole of far more volatile material having the same molecular weight (143.0 vs. 142.05 calcd.). Hydrolytic analysis of this gave 1.007Br^-, 5.024$B(OH)_3$, and 10.80H_2 per molecule. These results (and the absence of side reactions) prove the isomer.

Reversal of the isomerization was demonstrated by exposing 78 mg. of pure 2-BrB_5H_8 to $(CH_2)_6N_4$ (18 hr., 24°). The yield of 1-BrB_5H_8 was 12 mg. (15%) and the recovery of 2-BrB_5H_8 was 65 mg. (83%).

Physical Properties. As indicated by the data of Tables I and II, the isomers could be separated easily by high-vacuum fractional condensation. Melting ranges: 36.5-36.7° for 1-BrB_5H_8; for 2-BrB_5H_8, -56.0 to -55.7°.

Table I. Volatility of Liquid 1-BrB_5H_8

($\log P = 5.0374 + 1.75 \log T - 0.0033T - 2420/T$)

(t_{760} = 183.1°; Trouton constant = 20.9 e.u.)

Temp., °C.	36.5	45.9	50.8	56.0	61.8	70.0
P_{obsd}, mm.	3.63	6.03	7.80	10.12	13.31	19.50
P_{calcd}, mm.	3.63	6.05	7.79	10.11	13.37	19.50

Table II. Volatility of Liquid 2-BrB_5H_8

($\log P = 5.8959 + 1.75 \log T - 0.0045T - 2367/T$)

(t_{760} = 139.6°; Trouton constant = 21.16 e.u.)

Temp., °C.	17.80	30.85	34.45	38.50	52.75	59.60
P_{obsd}, mm.	5.82	12.20	14.80	18.35	36.9	50.0
P_{calcd}, mm.	5.80	12.24	14.82	18.31	36.7	50.0

The Dimethyl Ether Reactions. A reaction occurring during 3 days at 0° can be summarized as follows, with stoichiometry in mmoles.

$$1\text{-}BrB_5H_8 + (CH_3)_2O \rightarrow B_5H_9 + H_2 + CH_3Br + 2\text{-}BrB_5H_8$$

2.437	2.435	0.28	0.02	0.31	0.606
-1.237	-2.135				
1.200	0.300				

+ oily residue $(CH_3OB_5H_7Br)_x$

However, a 48-hr. run at 24° gave different results:

$$1\text{-}BrB_5H_8 + (CH_3)_2O \rightarrow B_5H_9 + H_2 + CH_3Br + 2\text{-}BrB_5H_8 + B(OCH_3)_3$$

3.275	3.377	1.135	0.035	1.434	0.535	0.27
-1.125	-2.000					
2.150	1.377					

+ $1\text{-}CH_3B_5H_8$ (trace) + $[(CH_3O)_3B_{17}H_{15}Br]_x$ (oily residue)

Then a 30-hr. process at 38° destroyed all BrB_5H_8 but gave a fair yield of $1\text{-}CH_3B_5H_8$ (characteristic infrared peaks, 1225, 1229, and 1232 $cm.^{-1}$; no appearance of $2\text{-}CH_3B_5H_8$ peaks at 1106, 1111, and 1154 $cm.^{-1}$); stoichiometry:

$$1\text{-}BrB_5H_8 + (CH_3)_2O \rightarrow H_2 + CH_4 + CH_3Br + 1\text{-}CH_3B_5H_8$$

0.995	1.01	0.72	0.72	0.31	0.29

+ residue $(CH_3B_5H_5BrO_{1.5})_x$

Comparison of the latter two experiments suggests that $B(OCH_3)_3$ served as a methylating agent. One may speculate whether the unknown $CH_3OB_5H_8$ was an unstable intermediate.

Methylpentaboranes. The $(CH_3)_2O$ reactions yielded $1\text{-}CH_3B_5H_8$ but no $2\text{-}CH_3B_5H_8$; apparently catalysts were lacking. The isomerization is irreversible, as shown by full recovery of $2\text{-}CH_3B_5H_8$ which had remained with $2,6\text{-}(CH_3)_2C_5H_3N$ for 5 days at 27°— conditions causing complete conversion of $1\text{-}CH_3B_5H_8$.[4] This isomerization, when catalyzed in the vapor

(4) T. P. Onak, J. Am. Chem. Soc., 83, 2584 (1961)

phase by $(CH_3)_2NB_2H_5$, does not depend upon transfer of BH_3 groups, for only 4% of a sample of 1-$CH_3B_5H_8$ isomerized during a one-boron B^{10}-B^{11} exchange with $(CH_3)_2NB_2H_5$ at 100°. This and other boron isotopic exchanges will be described more fully elsewhere.

For the volatility of 2-$CH_3B_5H_8$ (m.p. -55°), $\log P = 6.889 + 1.75 \log T - 0.0065T - 2212/T$ (accuracy like Table II; example, 19.0 mm. at 0°); thus it is roughly half as volatile as 1-$CH_3B_5H_8$ (34 mm. at 0°).[5]

(5) G. E. Ryschkewitsch *et al.*, *Inorg. Chem.*, 2, 891 (1963)

Infrared Spectra. The infrared peaks shown in Table III were recorded accurately by the Beckman IR7 instrument. After each frequency ($cm.^{-1}$) the relative intensity $k = (100/P)\log I_0/I$ (path 10 cm.; pressure P in mm. at 25°) is given in parentheses. Assignments are omitted because they would be either obvious or controversial.

(Insert Table III p. 5)

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Table III

Infrared Spectra of Pentaborane Derivatives

$1\text{-}BrB_5H_8$	$2\text{-}BrB_5H_8$	$1\text{-}CH_3B_5H_8$	$2\text{-}CH_3B_5H_8$
. . . .	. . . .	2975(0.54)	2975(1.5)
. . . .	. . . .	2940(0.65)	. . . .
. . . .	. . . .	2931(2.5)	2930(0.86)
. . . .	. . . .	2862(1.3)	2861(0.32)
2622(7.6)	2622(7.2)	2600(19)	2600(19)
2480(0.36)	2500(0.41)	. . . .	2440(0.12)
. . . .	. . . .	1996(0.13)	1940(0.27)
1850(1.8)	1800(0.58)	1840(2.0)	1855(0.93)
1804(0.89)	1718(0.24)	1790(1.3)	1811(0.97)
1625R(0.91)	1625R(0.46)	. . . .	. . . .
1602Q(1.10)	1603Q(0.87)	1629(0.34)	1600(0.17)
1585P(0.56)	1584P(0.43)	. . . .	. . . .
1442(2.3)	1393(5.5)	1418(2.9)	1435(4.4)
1386(1.6)	1342(0.81)	1386(2.9)	1386(4.9)
. . . .	. . . .	1330R(0.82)	1330R(1.5)
		1321Q(1.30)	1315Q(1.6)
. . . .	. . . .	1314P(0.46)	1310P(1.3)
		1262(0.32)	
. . . .	. . . .	1232Q(2.1)	1154(1.4)
		1229(1.9)	
1198(1.17)	. . . .	1225(1.8)	1111(0.65)
1152(2.5)	1120(0.93)	1168(0.20)	1106(0.68)
1065(0.82)	1029	1044R(0.28)	1036
1060(0.90)	1025 (3.8)	1036Q(0.52)	1031 (0.74)
1055(0.96)	1020	1026P(0.28)	1026
908(2.2)	887	907(5.9)	985(0.17)
861(1.1)	883 (3.5)		890(4.3)
	879	802(0.70)	
. . . .	856(1.55)	797(0.76)	. . . .
		791(0.70)	
764	764		
762 (1.64)	762 (0.63)	. . . .	. . . .
755	760		
648(2.8)	639(2.9)	643(5.1)	643(2.8)

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